

TOPIC 15 – ENERGETICS

15.1: STANDARD ENTHALPIES OF REACTION

IB Chemistry
T15D09



15.1 Standard enthalpy changes of reaction - 1.5 hour

- 15.1.1 Define and apply the terms standard state, standard enthalpy change of formation ΔH^θ_f and standard enthalpy change of combustion ΔH^θ_c . (2)
- 15.1.2 Determine the enthalpy change of a reaction using standard enthalpy changes of formation and combustion. (3)



15.1.1 – Terms

- 15.1.1 Define and apply the terms standard state, standard enthalpy change of formation ΔH_f^θ and standard enthalpy change of combustion ΔH_c^θ . (2)



15.1.1 – Enthalpy Δ of formation

- The **enthalpy change of formation**, ΔH^θ_f , of a substance is the heat change (at const P) on production of one mole of the pure substance from it's elements in their standard states under standard thermodynamic conditions (STP)
- The **standard state** is generally the most thermodynamically stable form of the pure element that exists at STP
 - For carbon, it's graphite (C(s))
 - For phosphorous, it's white phosphorous (P₄(s))



15.1.1 - Enthalpy Δ of formation

- Enthalpy change of formation of silver bromide, AgBr, is the enthalpy change of the reaction
 - $\text{Ag (s)} + \frac{1}{2} \text{Br}_2 \text{(l)} \rightarrow \text{AgBr (s)} \quad \Delta H^\theta_f = - 99.5 \text{ kJ/mol}$
- The following balanced equations do NOT represent enthalpy changes of formation:
 - $2 \text{Ag (s)} + \text{Br}_2 \text{(l)} \rightarrow 2 \text{AgBr (s)}$ (2 mol AgBr formed)
 - $\text{Ag (s)} + \frac{1}{2} \text{Br}_2 \text{(g)} \rightarrow \text{AgBr (s)}$ (Br is not std state)



15.1.1 - Enthalpy Δ of formation

- ΔH^\ominus_f (enthalpy changes of formation) are often hard to measure in practice due to many side reactions and slow rates of reaction.
- For example, CH_4 and KMnO_4 are prepared via the following:
 - $\text{C (s)} + 2 \text{H}_2 \text{(g)} \rightarrow \text{CH}_4 \text{(g)} \quad \Delta H^\ominus_f = -75 \text{ —}$
 - $\text{K (s)} + \text{Mn (s)} + 2 \text{O}_2 \text{(g)} \rightarrow \text{KMnO}_4 \text{(s)} \quad \Delta H^\ominus_f = -813 \text{ —}$
- Remember, we are in standard state, so formation of elements are zero (null reaction)
 - $\text{O}_2 \text{(g)} \rightarrow \text{O}_2 \text{(g)} \quad \Delta H^\ominus_f = 0 \text{ —}$
- However formation of ozone (O_3) and diamond (C) are not zero since these are not standard conditions!



15.1.1 - Enthalpy Δ of Combustion

- Some ΔH^θ_f are equal to the enthalpy of combustion.
- Remember, the **enthalpy of combustion** is the enthalpy change (at const P) when one mole of a pure substance undergoes complete combustion under standard thermodynamic conditions
- For water, $\Delta H^\theta_f = \Delta H_{\text{combustion}}$ of hydrogen
 - $\text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{l})$ $\Delta H^\theta_f = -286 \text{ —}$

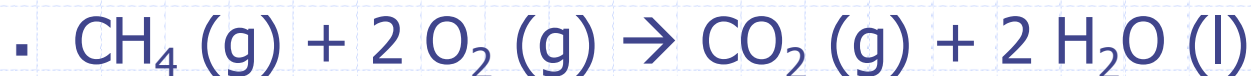


15.1.1 - Enthalpy Δ of Combustion

- For example, the standard enthalpies of combustion of hydrogen, methane, ethanol are:



- $\Delta H^\theta_{\text{c}} = -286 \text{ —}$



- $\Delta H^\theta_{\text{c}} = -890 \text{ —}$



- $\Delta H^\theta_{\text{c}} = -1370 \text{ —}$

- $\Delta H^\theta_{\text{f}}$ are usually calculated indirectly from other enthalpy changes of reaction (including bond enthalpies). $\Delta H^\theta_{\text{f}}$ often used to calc ΔH_{rxn} using Hess's Law.



15.1.1 – ΔH^\ominus_f exceptions

- Enthalpy changes of formation, ΔH^\ominus_f , are usually negative (exothermic) BUT some compounds have positive ΔH^\ominus_f such as benzene and nitrogen monoxide
 - $6\text{C (s)} + 3\text{H}_2\text{ (g)} \rightarrow \text{C}_6\text{H}_6\text{ (l)}$ $\Delta H^\ominus_f = +49\text{—}$
 - $\frac{1}{2}\text{N}_2\text{ (g)} + \frac{1}{2}\text{O}_2\text{ (g)} \rightarrow \text{NO (g)}$ $\Delta H^\ominus_f = +90\text{—}$
 - Such compounds are generally unstable relative to their elements. However, Gibbs free energy change of formation, ΔG^\ominus_f , is the criterion that determines the thermodynamic stability of a compound relative to its elements (15.4, almost there).



15.1.2 – Enthalpy Change

- 15.1.2 Determine the enthalpy change of a reaction using standard enthalpy changes of formation and combustion. (3)



15.1.2 - Enthalpy Δ of Reactions

- The enthalpy of any reaction can be determined by calculation, from the enthalpy changes of formation of all the substances in the chemical equation, using Hess's Law
- In words

Enthalpy change
of a reaction

=

Sum of
enthalpies of
formation of
products

-

Sum of enthalpies
of formation of
reactants

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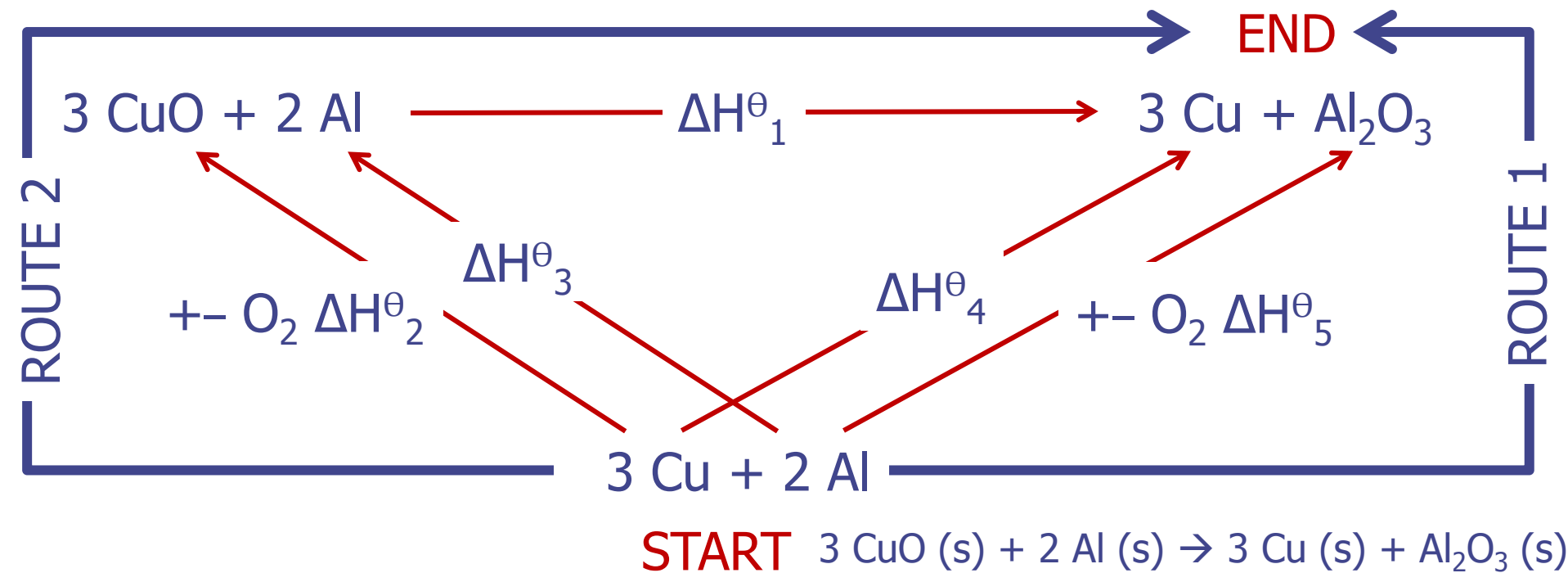
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15.1.2 - Enthalpy Δ of Reactions

- Calculate the enthalpy change of the following reaction:
 - $3 \text{ CuO (s)} + 2 \text{ Al (s)} \rightarrow 3 \text{ Cu (s)} + \text{Al}_2\text{O}_3 \text{ (s)}$
 - $\Delta H^\theta_f [\text{CuO}] = -155 \text{ —}$
 - $\Delta H^\theta_f [\text{Al}_2\text{O}_3] = -1669 \text{ —}$
 - This is a redox rxn (Topic 09) and involves a more reactive metal displacing a less reactive metal from its oxide





$$\Delta H^\theta_f [\text{CuO}] = -155 \text{ —}$$

$$\Delta H^\theta_f [\text{Al}_2\text{O}_3] = -1669 \text{ —}$$

- Applying Hess's Law:

- Enthalpy change in route 1 = enthalpy change in route 2

- $\Delta H^\theta_2 + \Delta H^\theta_3 + \Delta H^\theta_1 = \Delta H^\theta_4 + \Delta H^\theta_5$

- $\Delta H^\theta_1 = \Delta H^\theta_4 + \Delta H^\theta_5 - \Delta H^\theta_2 - \Delta H^\theta_3$

- $\Delta H^\theta_1 = (0 \text{ —}) + (-1669 \text{ —}) - 3(-155 \text{ —}) - (0 \text{ —}) = -1204 \text{ —}$

- $[\quad] \quad [\quad]$

15.1.2 – $\Delta H^{\theta}_{\text{rxn}}$ from $\Delta H^{\theta}_{\text{c}}$

- Enthalpy changes of reaction from enthalpy changes of combustion
- Enthalpy can also be calculated from enthalpy changes of combustion. However, this can only be done for reactions in which the substances on both sides of the equation can be burnt in oxygen
- This method is widely used for organic compounds



15.1.2 – $\Delta H^{\theta}_{\text{rxn}}$ from $\Delta H^{\theta}_{\text{c}}$

- Example:
 - Calculate the enthalpy change of reaction for the hydrogenation of propene to form propane
 - $\text{CH}_3\text{-CH=CH}_2 (\text{g}) + \text{H}_2 (\text{g}) \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_3 (\text{g})$
 - $\Delta H^{\theta}_{\text{c}} [\text{C}_3\text{H}_6 (\text{g})] = -2509 \text{ —}$
 - $\Delta H^{\theta}_{\text{c}} [\text{H}_2 (\text{g})] = -286 \text{ —}$
 - $\Delta H^{\theta}_{\text{c}} [\text{C}_3\text{H}_8 (\text{g})] = -2220 \text{ —}$
 - Work example on your sheet



15.1.2 – ΔH^θ of atomization

- The **enthalpy of atomization** of an element is the heat change (at const P) when one mole of separate gaseous atoms of the element is formed from the element (in its standard state) at STP
- The following thermochemical equations each describe the enthalpy of atomization of an element. In each case the enthalpy change of the reaction is equivalent to the enthalpy change of atomization



For halogen = $\frac{1}{2}$ bond enthalpy!

15.1.2 – ΔH^θ of atomization

- $\Delta H^\theta_{\text{at}}$ of noble gases always zero, since elements are already in the form of separate gaseous atoms under STP
- $\Delta H^\theta_{\text{at}}$ are always positive b/c energy must be absorbed to pull the atoms apart and overcome the chemical bonds
- $\Delta H^\theta_{\text{at}}$ are usually found indirectly by calculation from other enthalpy changes, using Hess's Law
- $\Delta H^\theta_{\text{at}}$ are used in the Born-Haber cycle calculations in section 15.2 (next class!)



15.1.2 – ΔH^θ of physical change

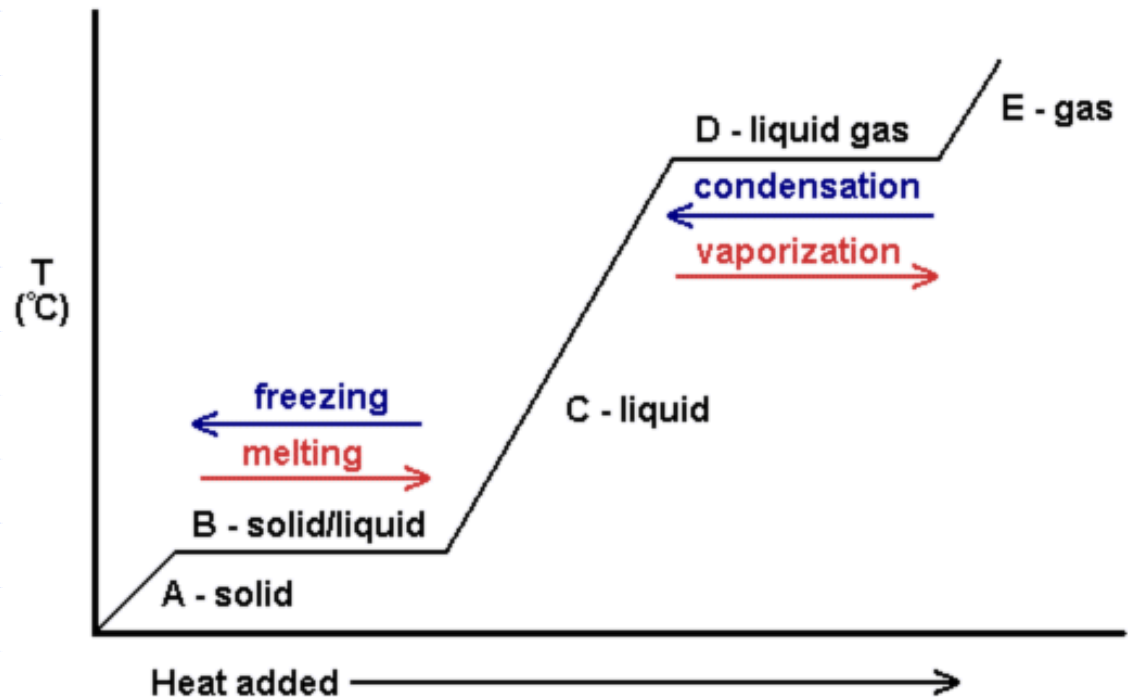
- The standard enthalpy change that accompanies a change in physical state is called the **standard enthalpy of transition**. Two examples are:
 - Standard enthalpy of fusion
 - The enthalpy change which occurs (at cons. P) when one mole of a pure solid is completely melted under standard conditions
 - Standard enthalpy of vaporization
 - The enthalpy change which occurs (at const. P) when one mole of a pure liquid is completely vaporized at STP.



Phase Changes: does $q = mc\Delta T$ work?

- What happens to the temperature while water boils?
- When it snows in mild climates (like many cities on the west coast of the US) why does the temperature linger about 0°C ?

If $\Delta T = 0^{\circ}\text{C}$ then the entire value of $q = 0$ using $mc\Delta T$. But we know that it takes energy...so we use another equation during phase change.



15.1.2 - Phase Change Equation

- When a substance changes phase or state (solid to liquid, liquid to gas) it needs energy to occur.
 - This energy does not raise the temperature but instead is used to break the intermolecular forces sufficiently so that the solid liquefies or the liquid vaporizes.
 - In the reverse process energy has to be given off for a gas to liquefy or a liquid to solidify.
- We can measure this by the phase change equation $q = m \times H_{\text{vap}}$ or $q = m \times H_{\text{fus}}$
 - Vaporization for liquid/gas interface
 - Fusion for liquid/solid interface

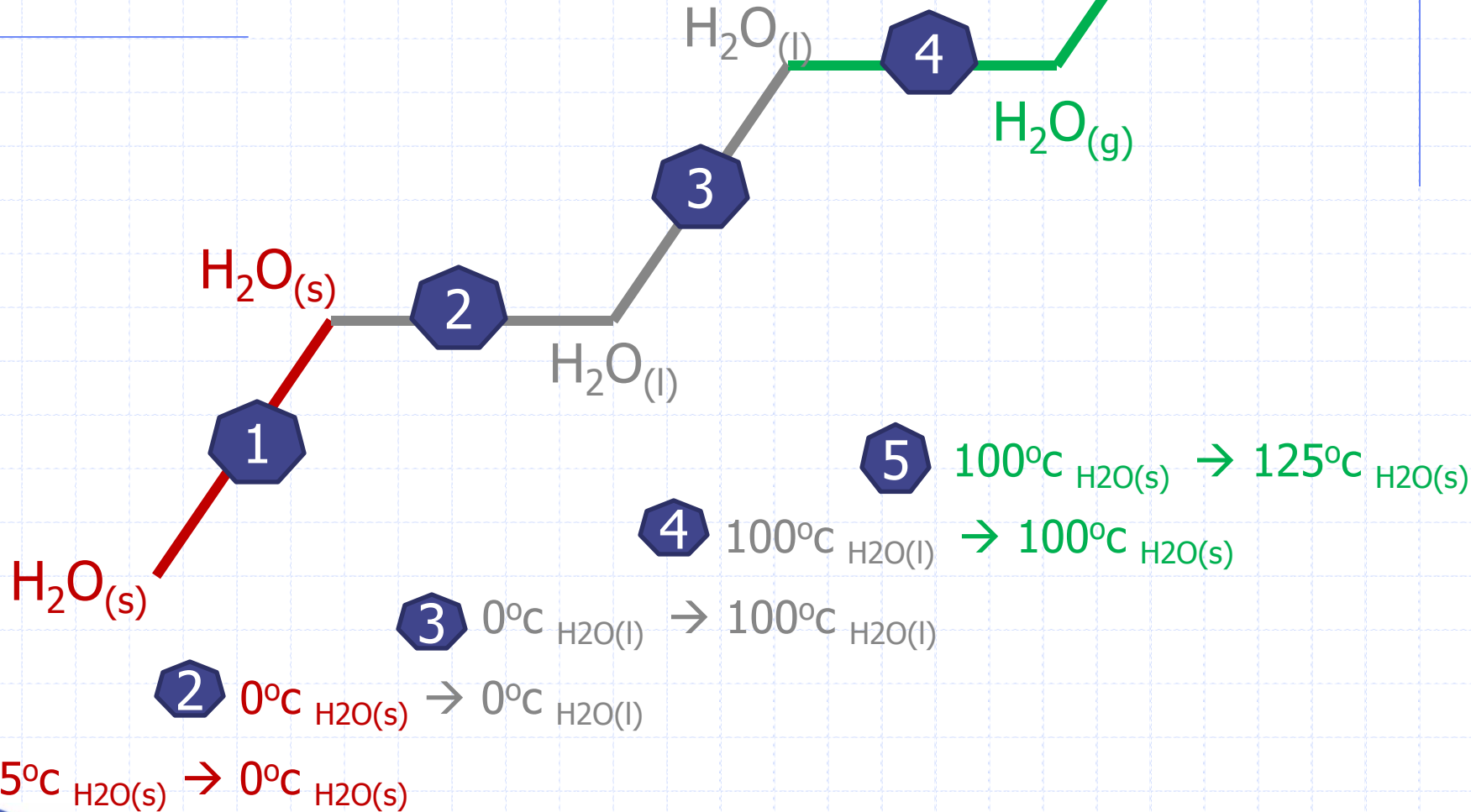


15.1.2 - Water as an example:

- In the liquid/gas interface:
 - $q = m \times H_{\text{vap}}(\text{H}_2\text{O})$
 - $\text{L} \rightarrow \text{G}$: $H_{\text{vap}}(\text{H}_2\text{O})$ is $-(2260) \text{ J/g}$.
 - $\text{G} \rightarrow \text{L}$: $H_{\text{vap}}(\text{H}_2\text{O})$ is 2260 J/g .
- In the liquid/solid interface:
 - $q = m \times H_{\text{fus}}(\text{H}_2\text{O})$
 - $\text{S} \rightarrow \text{L}$: $H_{\text{fus}}(\text{H}_2\text{O})$ is $-(333) \text{ J/g}$
 - $\text{L} \rightarrow \text{S}$: $H_{\text{fus}}(\text{H}_2\text{O})$ is 333 J/g



For example, if ice ($\text{H}_2\text{O}_{(s)}$) at -25°C is heated to water vapor ($\text{H}_2\text{O}_{(g)}$) at 125°C , the following phase change occurs....



For water:

H_{fus} (fusion) =

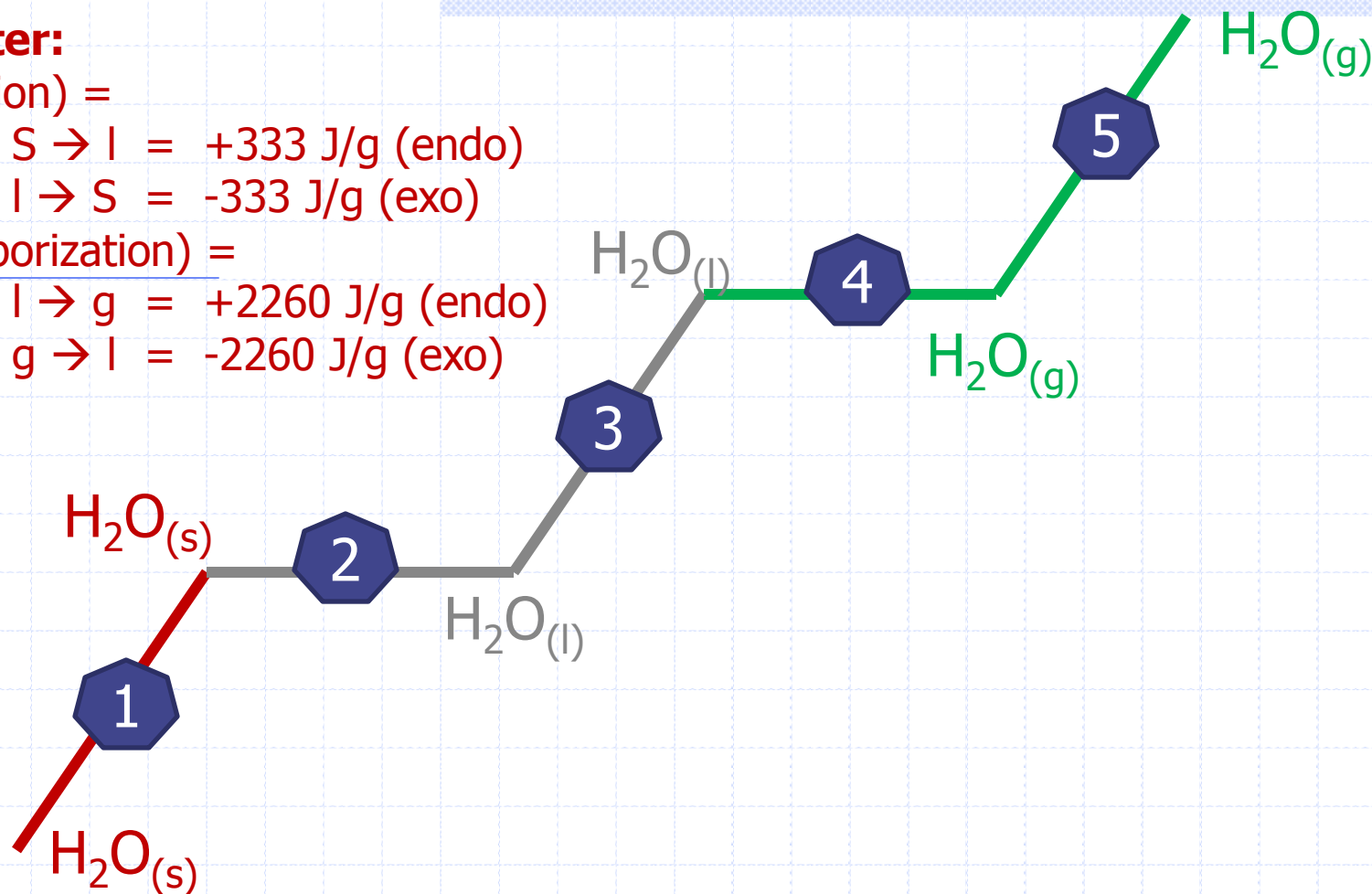
$$S \rightarrow L = +333 \text{ J/g (endo)}$$

$$L \rightarrow S = -333 \text{ J/g (exo)}$$

H_{vap} (vaporization) =

$$L \rightarrow g = +2260 \text{ J/g (endo)}$$

$$g \rightarrow L = -2260 \text{ J/g (exo)}$$



- Change in **temperature** for solid (s), liquid (l), gas (g)

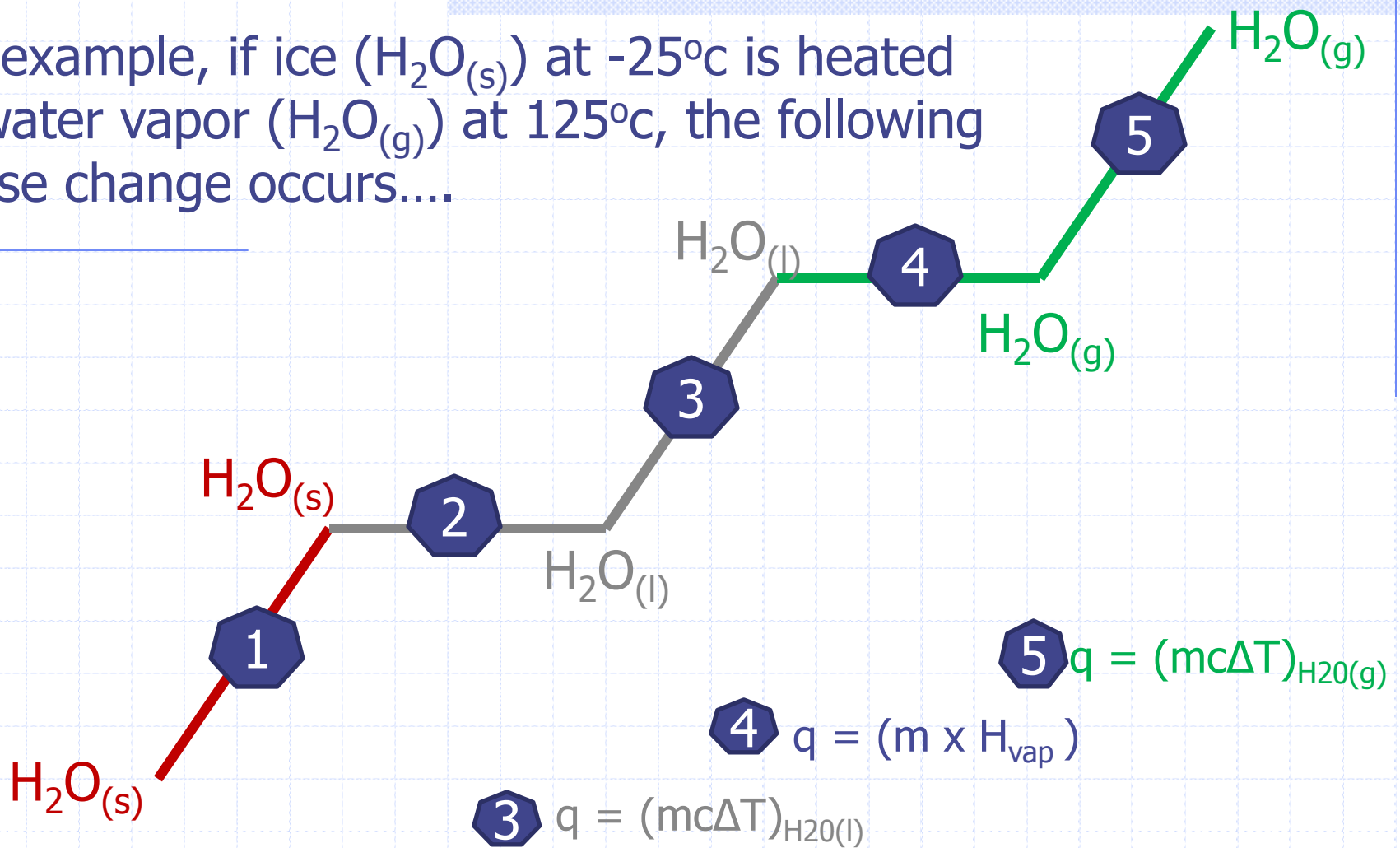
- Use $q = mc\Delta T$

- Change in **phase** (s \rightarrow l), (l \rightarrow g), or the reverse

- Use $q = m \times H_{\text{fus}}$ or $q = m \times H_{\text{vap}}$



For example, if ice ($\text{H}_2\text{O}_{(s)}$) at -25°C is heated to water vapor ($\text{H}_2\text{O}_{(g)}$) at 125°C , the following phase change occurs....



$$5 \quad q = (mc\Delta T)_{\text{H}_2\text{O}_{(g)}}$$

$$4 \quad q = (m \times H_{\text{vap}})$$

$$3 \quad q = (mc\Delta T)_{\text{H}_2\text{O}_{(l)}}$$

$$2 \quad q = (m \times H_{\text{fus}})$$

$$1 \quad q = (mc\Delta T)_{\text{H}_2\text{O}_{(s)}}$$

$$q_{\text{total}} = (mc\Delta T)_{\text{H}_2\text{O}_{(s)}} + (m \times H_{\text{fus}}) + (mc\Delta T)_{\text{H}_2\text{O}_{(l)}} + (m \times H_{\text{vap}}) + (mc\Delta T)_{\text{H}_2\text{O}_{(g)}}$$



Units to know for water:

- These would be provided on an exam:

Specific heat of water	$4.184 \text{ Jg}^{-1}\text{°C}^{-1}$
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Specific heat of ice	$2.00 \text{ Jg}^{-1}\text{°C}^{-1}$
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Specific heat of steam	$2.04 \text{ Jg}^{-1}\text{°C}^{-1}$
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Heat of fusion of ice	333 J/g
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Heat of vaporization of water	2260 J/g
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Density of water	1.00 g/mL
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